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(54) **SUPPORTED MO—O—K—ME_xO_y CATALYST FOR THE SYNTHESIS OF METHANETHIOL FROM HIGH H₂S-CONTAINING SYNGAS**

(75) Inventors: **Yiquan Yang**, Xiamen (CN); **Yingjuan Hao**, Xiamen (CN); **Aiping Chen**, Xiamen (CN); **Qi Wang**, Xiamen (CN); **Lingmei Yang**, Xiamen (CN); **Qiaoling Li**, Xiamen (CN); **Shenjun Dai**, Xiamen (CN); **Weiping Fang**, Xiamen (CN); **Jan-Olaf Barth**, Frankfurt (DE); **Christoph Weckbecker**, Gruendau-Lieblos (DE); **Klaus Huthmacher**, Gelnhausen (DE)

(73) Assignee: **EVONIK DEGUSSA GMBH**, Essen (DE)

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Primary Examiner — Jun Li

(74) Attorney, Agent, or Firm — Smith, Gambrell & Russell, LLP

(57) **ABSTRACT**

This invention is related to a preparation method of a supported catalyst Mo—O—K—Me_xO_y for the synthesis of methanethiol from H₂S-containing syngas. The catalyst comprises of an active component of Mo—O—K-based species, an active promoter and a support denoted as metal (or metals)-carrier. The support is prepared by electroless plating method in such a way that the metal or metals chosen are plated onto the surface of the carrier. Transition metal, especially Fe, Co or Ni are selected to be the plating metal, while SiO₂, Al₂O₃ or TiO₂ are selected to be carrier. The catalyst thus prepared is found to be efficient for the synthesis of methanethiol from H₂S-containing syngas or carbon oxides/hydrogen mixtures, especially regarding a minor formation of the by-product CO₂.

12 Claims, No Drawings

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SUPPORTED MO—O—K—Me_xO_y CATALYST FOR THE SYNTHESIS OF METHANETHIOL FROM HIGH H₂S-CONTAINING SYNGAS

The present invention relates to a preparation method of a supported Mo—O—K—Me_xO_y catalyst for the synthesis of methanethiol from high H₂S-containing syngas, therein support is a metal (or metals)-plated carrier, especially metal (or metals)-plated-SiO₂, which is made by electroless plating method.

THE PRIOR ART

As an important chemical material used to produce methionine, pesticides and medicine, methanethiol is predominantly prepared by the reaction of hydrogen sulfide with methanol. The direct synthesis of methanethiol from the reaction of H₂S with carbon oxides, in particular, from H₂S-containing syngas is an attractive alternative. For example, EP167,354 disclosed a synthesis pathway from the reaction of hydrogen sulfide with carbon monoxide in the presence of a catalyst NiO or MoO₃ supported on TiO₂; Chinese patent CN98118186.4 and CN98118187.2 disclosed Mo—S—K/SiO₂ catalysts used for methanethiol synthesis from high H₂S-containing syngas; Chinese patent appl.200310100496.1 and 200310100495 reported Mo—O—K/SiO₂ catalysts promoted by transition metal oxides or rare earth metal oxides for the methanethiol synthesis, herein the promoters were selected from the oxides of Co, Ni, Fe, Mn or the rare earth oxides of La, Ce, the active component Mo—O—K base are formed from the precursor K₂MoO₄ or (NH₄)₆Mo₇O₂₄·4H₂O plus potassium salt. Those catalysts were prepared by traditional impregnation method. The catalysts exhibit high selectivity and space-time-yield of methyl mercaptan, but produce also by-products, such as carbonyl sulfide, methane and dimethyl sulfide.

STATEMENT OF THE INVENTION

The object of this invention is to develop a further improved solid supported Mo—O—K—Me_xO_y catalyst with high activity and selectivity of methanethiol, but lower selectivity of CO₂.

DETAILED DESCRIPTION OF THE INVENTION

The object of the invention is a catalyst comprising:

- a support, consisting of a porous carrier and a metal A deposited thereon by electroless deposition of metal on the carrier;
- a Mo—O—K based active component; and
- optionally an active promoter Me_xO_y, chosen from the group of transition metal oxides or rare earth metal oxides or rare earth metal oxides, wherein x and y depend on the valence of the metal.

The catalyst comprises an active component, optionally an active promoter and a support. Said active component is a Mo—O—K-based component. Said promoter is at least one chosen from the group of transition metal oxides, or rare earth metal oxides, comprising especially from the oxides of iron, cobalt, Nickel, manganese, lanthanum and cerium, and expressed as Me_xO_y, wherein "Me" denotes the metal selected from the group of transition metals of rare earth metals, especially Fe, Co, Ni, Mn, La or Ce.

Said support is a metal (or metals)-plated carrier, especially metal (or metals)-SiO₂, which is made by electroless plating method. In general the carrier used is porous and

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chosen from the group of SiO₂, Al₂O₃, TiO₂, Zeolites, especially SiO₂. Said metal or metals plated on said carrier can be selected from the group of Ni, Co or Fe, preferably Ni or Co.

When potassium molybdate is used as precursor of the Mo—O—K-based component, the catalyst of present invention is denoted as K₂MoO₄-Me_xO_y/Metal-carrier, wherein the weight ratios of the components of the catalyst are

$$\text{K}_2\text{MoO}_4/\text{Me}_x\text{O}_y/\text{metal-carrier}=(1-30)/(0.0-25.0)/(0.1-10.0)-100, \text{ preferably } (15-20)/(0.0-25.0)/(0.5-8.0)-100;$$

when (NH₄)₆Mo₇O₂₄·4H₂O plus one of potassium salts or MoO₃ plus one of potassium salts serve as precursors of the Mo—O—K-based compound, the catalyst of the present invention is expressed as MoO₃—K₂O—Me_xO_y/metal-carrier, wherein the weight ratios of the components of the catalyst are:

$$\text{MoO}_3/\text{K}_2\text{O}/\text{Me}_x\text{O}_y/\text{metal-carrier}=(1-30)/(1-20)/(0.0-25.0)/(0.1-10.0)-100, \text{ preferably } (15-20)/(10-15)/(0.0-25.0)/(0.5-8.0)-100;$$

Said potassium compound is at least one chosen from the group, comprising

K₂CO₃, KOH, KNO₃ and CH₃COOK.

Chemically metal-plating method is used to prepare said metal (or metals)-carrier the metal (or metals) chosen is plated onto the carrier chosen, wherein the weight ratio of metal (or metals)/carrier is (0.1-10.0)/100, preferably (0.5-8.0)/100.

The invention is also directed to the preparation of said catalysts by multi-step impregnation.

In order to distribute the active component more equally over the support, at least one chelating reagent should be used in the impregnation process.

Said chelating or coordinating reagent is at least one chosen from the group comprising citric acid, ammonium citrate, L-glutamic acid, tartaric acid and ethylenediaminetetraacetic acid(EDTA); the amount of chelating agent added correspondingly is 0.1-0.6 times as much by weight as that of the support, more preferably is 0.3-0.6 times as much as that of the support. Suitable amounts of ammonia are added to adjust the pH value of the steeping liquor to 7.0-13.0, preferable 8.0-12.0.

The activation of the carrier by chemically plating metal proceeds as follows (shown as a preferred method):

(1) the preparation of metal-plating solution:

A given quantity of soluble metal salt chosen and a given quantity of coordinating agent are dissolved in a given quantity of distilled water successively to produce a metal-plating solution, in which the concentration of the metal ions varies from 1 g/l to 20 g/l, preferably 5-7 g/l; the coordinating agent is at least one chosen from Na₃C₆H₅O₇·2H₂O, C₆H₈O₇·H₂O, C₂H₈N₂ or NaKC₄H₄O₆·4H₂O, the concentration of the coordinating agent varies from 1 g/l to 20 g/l.

Keeping stirring for 10 minutes, then a given quantity of the stabilizing agents (NH₄)₂SO₄ or Na₃C₆H₅O₇·2H₂O, is added subsequently to the plating solution obtained above followed by stirring for another 20 minutes, followed by adding some NH₃·H₂O to adjust the pH of the plating solution to 7.0-13.0, preferably 8.0-12.0; finally, a suitable amount of distilled water is added to adjust the volume of the solution in such a way that the concentration of metal salt chosen in the plating solution varies from 1 g/l to 20 g/l, preferably 5-7 g/l.

(2) Pretreatment of the carrier:

Prior to plating the metal onto the carrier, the carrier is preferably pretreated by the following processes:

a) the carrier should be washed with distilled water, and then dried, followed by immersing the clean carrier in a solution of 4.5 mol/l H_2SO_4 +0.88 mol/l H_2O_2 (1:1) for 5 minutes under agitating, and subsequently washed with distilled water three times;

b) the cleaned carrier is immersed in an aqueous solution of activation agent under agitation, said activation agent is preferably PdCl_2/HCl , the concentration of the activation agent varies in general from 0.05 g/l to 1.0 g/l, preferably from 0.1 g/l to 0.5 g/l; keeping ultrasonically agitating for e.g. 30-35 minutes, then washing with distilled water three times;

c) the activated carrier is immersed in an aqueous solution of a reducing agent under agitation; the reducing agent is preferably NaH_2PO_4 or NaBH_4 ; the concentration of the agent varies from 20 g/l to 30 g/l;

(3) Plating of metal onto carrier is conducted by putting the pretreated carrier produced in step (2) into the plating solution of the metal chosen at 40-85° C. for 30-40 minutes. The metal-plated carrier is washed with distilled water e.g. for three times and then dried at about 110° C. for about 6 hours. The metal-plated carrier is termed support, such as support Ni-SiO_2 or Co-SiO_2 .

Impregnation of the Support with the Active Component (Shown as a Preferred Method)

(1) A given quantity of said precursor K_2MoO_4 or $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ plus a potassium salt or MoO_3 plus a soluble potassium compound and suitable amount of chelating agent are dissolved in distilled water to generate an impregnation solution; into which then a suitable amount of $\text{NH}_3\cdot\text{H}_2\text{O}$ is dropped to adjust the pH of the impregnation solution at 8-12, preferably 8-10; then the metal-plated carrier (30-45 meshes) produced in step (3) of carrier activation is soaked in the impregnation solution at room temperature for 12 hours, then dried at 120° C. for 5 hours to produce the desired supported Mo-O-K catalyst.

(2) Alternatively, a given quantity of said precursor K_2MoO_4 or $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ plus a soluble potassium compound or MoO_3 plus a potassium salt are dissolved in distilled water, then a suitable amount of $\text{NH}_3\cdot\text{H}_2\text{O}$ is dropped into the solution to make the precursor fully dissolved in the distilled water to generate an impregnation solution, which contains only an active component.

In a preferred case a given quantity of soluble transition metal salt or rare earth metal salt chosen, especially, its sulfate, nitrate or acetate, and suitable amount of chelating agent are added to the above described solution, into which a suitable amount of $\text{NH}_3\cdot\text{H}_2\text{O}$ is then dropped to adjust the pH of the impregnation solution at 8-12, preferably 8-10; lastly the metal (or metals)-plated carrier (30-45 meshes) produced in step (3) of carrier activation is soaked in the impregnation solution at room temperature for 12 hours, then filtered and dried at 110° C. for 6 hours to produce the desired supported $\text{Mo-O-K-Me}_x\text{O}_y$ catalyst.

Said catalyst is used for a method to prepare methanethiol from high H_2S -containing syngas. The reaction conditions are known from the state of art.

The catalyst should be sulfided for 8-10 h before using.

The reactivity evaluation of the catalyst of present invention was carried out in a fixed-bed tubular reactor with 0.5 ml of catalyst per pass. The reaction conditions are preferably $\text{CO}/\text{H}_2/\text{H}_2\text{S}=1/1/2$, 250-350° C., about 0.05-0.3 MPa and $\text{GHSV}=500\text{-}3000\text{ h}^{-1}$. The products were analyzed by GC. All data were taken after the steady state achieved.

The assay results show that the catalyst of the present invention were not only has high catalytic activity for the synthesis of methanethiol from high H_2S -containing syngas, but also has high selectivity of methanethiol, but less selectivity of CO_2 .

The following examples illustrate the present invention further.

Example 1

Electroless Plating

(1) 2.0 g of $\text{NiSO}_4\cdot 7\text{H}_2\text{O}$ and 2.0 g of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7\cdot 2\text{H}_2\text{O}$ were dissolved in 50 ml of distilled water successively to produce a plating solution, keeping stirring for 10 minutes, then 3.0 g of $(\text{NH}_4)_2\text{SO}_4$ and 3.0 g of $\text{NaH}_2\text{PO}_4\cdot \text{H}_2\text{O}$ were added one after another to the solution obtained above, stirring for another 20 minutes, followed by adding some $\text{NH}_3\cdot\text{H}_2\text{O}$ to adjust the pH of the solution to 9.0; finally, distilled water was added to adjust the volume of the solution to 100 ml in such a way that the concentration of NiSO_4 in the plating solution is 20 g/l;

(2) 10 g of clean SiO_2 was immersed in 20 ml of 4.5 mol/l H_2SO_4 +0.88 mol/l H_2O_2 (1:1) solution for 5 minutes under agitating, and then washed for three times with distilled water; followed by immersing the carrier SiO_2 in 20 ml of 0.1 g/l PdCl_2/HCl solution, keeping ultrasonically agitating for 30 minutes, and then washed for three times with distilled water; the next step was to immerse the activated carrier SiO_2 in 10 ml of 30 g/l NaH_2PO_4 solution, at the same time agitating for 10 seconds and repeated the reduced experiment step again, so as to form an activated carrier.

(3) The electroless plating process was carried out by immersing the activated carrier SiO_2 in the plating solution prepared in step (2) at appr. 40° C. for 30 minutes. After plating, the Ni-plated SiO_2 was washed with distilled water three times and dried at 383K for 4 h. The weight ratio of metal over carrier of the support thus prepared was $\text{Ni-SiO}_2=4.4\text{-}100$.

(4) 0.45 g of K_2MoO_4 and 3.0 g of tartaric acid were dissolved in 6 ml of distilled water to generate an impregnation solution, into which then 0.8 ml of $\text{NH}_3\cdot\text{H}_2\text{O}$ was dropped to adjust the pH of the impregnation solution at 9. Then 3 g of support Ni-SiO_2 (30-45 meshes) produced in step (3) was soaked in the impregnation solution at room temperature for 12 hours, then dried at 110° C. for 5 hours. The weight ratio of every component of the catalyst was $\text{K}_2\text{MoO}_4/\text{Ni-SiO}_2=15/(4.4\text{-}100)$. The evaluation result of the catalyst thus prepared is shown in table 1.

Example 2, 3, 4

The catalysts were prepared according to the experiment steps described in Example 1, but the concentration of the plating solution was respectively diluted by once, twice three times with distilled water, namely the nickel ion concentration was respectively 10 g/l, 6.67 g/l, 5 g/l. The weight ratio of every content of the catalysts gained was $\text{K}_2\text{MoO}_4/\text{Ni-SiO}_2=15/(2.2\text{-}100)$, $\text{K}_2\text{MoO}_4/\text{Ni-SiO}_2=15/(1.5\text{-}100)$, $\text{K}_2\text{MoO}_4/\text{Ni-SiO}_2=15/(1.1\text{-}100)$ respectively. The evaluation results of the catalysts thus prepared were also shown in table 1.

Example 5, 6

The catalysts were prepared according to the experiment steps described in Example 1, but the weight of carrier SiO_2 to

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be plated was respectively 8 g and 6 g. The weight ratio of every content of the catalysts gained was $K_2MoO_4/Ni-SiO_2=15/(5.5-100)$ and $K_2MoO_4/Ni-SiO_2=15/(7.3-100)$, respectively. The evaluation results of the catalysts thus prepared are also shown in table 1.

TABLE 1

performance of the catalysts $K_2MoO_4/Ni-SiO_2$ in examples 1-6							
ex- am- ples	$K_2MoO_4/Ni-SiO_2$	selectivity				CO_2/CH_3SH	CO % conver- sion
		CH_4	CH_3SH	COS	CO_2	CH_3SH	
1	15/(4.4-100)	0.0226	46.84	18.91	34.02	0.7265	56.84
2	15/(2.2-100)	0.0216	46.31	20.33	33.14	0.7156	63.45
3	15/(1.5-100)	0.0202	46.61	20.67	32.70	0.7017	65.61
4	15/(1.1-100)	0.0130	43.37	24.91	31.70	0.7311	49.16
5	15/(5.5-100)	0.0207	46.70	19.01	34.27	0.7338	56.57
6	15/(7.3-100)	0.0196	46.85	19.14	34.99	0.7255	55.46

Example 7, 8, 9, 10, 11

The catalysts were prepared according to the experiment steps described in Example 3, but the weight ratio of $K_2MoO_4/support$ varied from 5/100, 10/100, 15/100, 20/100, 25/100. The weight ratio of every component of the catalysts gained was $K_2MoO_4/Ni-SiO_2=5/(1.5-100)$, $K_2MoO_4/Ni-SiO_2=10/(1.5-100)$, $K_2MoO_4/Ni-SiO_2=15/(1.5-100)$, $K_2MoO_4/Ni-SiO_2=20/(1.5-100)$, $K_2MoO_4/Ni-SiO_2=25/(1.5-100)$ respectively. The evaluation results of the catalysts thus prepared were also shown in table 2.

Example 12

(1) 0.667.0 g of $NiSO_4 \cdot 7H_2O$ and 0.667 g of $Na_3C_6H_5O_7 \cdot 2H_2O$ were dissolved into 50 ml of distilled water successively to produce a plating solution, keeping stirring for 10 minutes, then 1.0 g of $(NH_4)_2SO_4$ and 1.0 g of $NaH_2PO_4 \cdot H_2O$ were added one after another to the solution obtained above, stirring for another 20 minutes, followed by adding some $NH_3 \cdot H_2O$ to adjust the pH of the solution to 9.0; finally, distilled water was added to adjust the volume of the solution to 100 ml in such a way that the concentration of $NiSO_4$ in the plating solution was 4.12 g/l;

(2) 10 g of clean SiO_2 were immersed in 20 ml of 4.5 mol/l $H_2SO_4+0.88$ mol/l $H_2O_2(1:1)$ solution for 5 minutes under agitating, and then washed for three times with distilled water, followed by immersing the carrier SiO_2 in 20 ml of 0.1 g/l $PdCl_2/HCl$ solution, at the same time keeping ultrasonically agitating for 30 minutes, and then washed for three times with distilled water; the next step was to immerse the activated carrier SiO_2 in 10 ml of 30 g/l NaH_2PO_4 solution, at the same time agitating for 10 seconds; finely repeated the reduced experiment step again to produce an activated carrier SiO_2 .

(3) The electroless plating process was carried out by immersing the activated carrier SiO_2 in the plating solution prepared in step (2) at 42° C. for 30 minutes. After plating, the Ni-plated SiO_2 was washed with distilled water four times and then dried at 110° C. for 6 hours. The weight ratio of the two contents of the support thus prepared was $Ni-SiO_2=1.5-100$.

(4) 0.496 g of K_2MoO_4 and 1.0 ml of $NH_3 \cdot H_2O$ were dissolved in 5 ml of distilled water to generate an impregnation solution; then 0.5 g of tartaric acid and 0.135 g of $Ni(NO_3)_2 \cdot 6H_2O$ were added to the K_2MoO_4 solution, the pH

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value of the K_2MoO_4 solution was measured to be at 9; then 3 g of support nickel-plated SiO_2 (30-45 meshes) produced in step (3) was soaked in the impregnation solution at room temperature for 12 hours, then dried at 110° C. for 6 hours.

The weight ratio of every component of the catalyst thus prepared was $K_2MoO_4/NiO/Ni-SiO_2=15/1.0/(1.5-100)$. The evaluation result of the catalyst thus prepared is shown in table 3.

Example 13

The catalyst was prepared according to the experiment steps described in Example 12, but 0.1346 g of $Co(NO_3)_2 \cdot 6H_2O$ substituted for 0.135 of $Ni(NO_3)_2 \cdot 6H_2O$. The weight ratio of every component of the catalyst thus prepared was $K_2MoO_4/CoO/Ni-SiO_2=15/1.0/(1.5-100)$. The evaluation result of the catalyst thus prepared is also shown in table 3

Example 14

The catalyst was prepared according to the experiment steps described in Example 1, but $NiSO_4 \cdot 7H_2O$ for preparing plating solution was replaced by $CoSO_4 \cdot 7H_2O$, the amount of $CoSO_4 \cdot 7H_2O$ is the same as that of $NiSO_4 \cdot 7H_2O$, but the Ph value of the plating solution was adjusted by $NH_3 \cdot H_2O$ to 12; the plating process of the activated carrier SiO_2 was carried out at 80° C. The weight ratio of every component of the catalyst gained was $K_2MoO_4/(Co-SiO_2)=15/(4-100)$. The evaluation result of the catalyst thus prepared was shown in table 4

Example 15

The catalyst was prepared according to the experiment steps described in Example 12, but 0.667 g of $NiSO_4 \cdot 7H_2O$ for preparing plating solution was replaced by 0.667 g of $CoSO_4 \cdot 7H_2O$; while the quantity of $Ni(NO_3)_2 \cdot 6H_2O$ for preparing promoter Me_xO_y was 0.117 g. The weight ratio of every component of the catalyst gained was $K_2MoO_4/NiO/Co-SiO_2=15/1/(1.5-100)$. The evaluation result of the catalyst thus prepared is also shown in table 4

Example 16

The catalyst was prepared according to the experiment steps described in Example 15, but 0.117 g of $Ni(NO_3)_2 \cdot 6H_2O$ for preparing promoter Me_xO_y was replaced by 0.117 g of $Co(NO_3)_2 \cdot 6H_2O$. The weight ratio of every component of the catalyst gained was $K_2MoO_4/CoO/Co-SiO_2=15/1/(1.5-100)$. The evaluation result of the catalyst thus prepared is also shown in table 4

Example 17

The catalyst was prepared according to the experiment steps described in Example 1, but 0.45 g K_2MoO_4 and 0.5 g tartaric acid were replaced by 3.00 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ plus 0.45 g of KNO_3 and 0.5 g of citric acid respectively. The weight ratio of every component of the catalyst gained was $MoO_3/K_2O/(Ni-SiO_2)=11/4/(4-100)$. The evaluation result of the catalyst thus prepared is shown in table 5

Example 18

The catalyst was prepared according to the experimental steps described in Example 12, but 0.496 g K_2MoO_4 was replaced by 3.00 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ plus 0.22 g of

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K₂CO₃. The weight ratio of every component of the catalyst gained was MoO₃/K₂O/NiO/(Ni—SiO₂)=11/4/0.25/(1.5-100). The assay result of the catalyst thus prepared was shown in table 5.

TABLE 2

performance of catalysts K ₂ MoO ₄ /Ni—SiO ₂ in examples 7-11							
ex- am- ples	K ₂ MoO ₄ / (Ni—SiO ₂)	Selectivity, %					CO Con- ver- sion, %
		CH ₄	CH ₃ SH	COS	CO ₂	CH ₃ SH	
7	5/(1.5-100)	0.0956	28.74	40.12	31.04	1.080	30.21
8	10/(1.5-100)	0.0353	38.13	28.64	33.20	0.871	43.15
9	15/(1.5-100)	0.0282	46.61	16.79	36.57	0.785	65.61
10	20/(1.5-100)	0.0339	35.96	33.47	30.23	0.841	58.96
11	25/(1.5-100)	0.0496	30.38	38.24	31.33	1.030	59.63

TABLE 3

performance of catalysts K ₂ MoO ₄ —NiO/Ni—SiO ₂ in examples 10-11							
examples	catalysts	Selectivity, %				CO ₂ /CH ₃ SH	CO % conversion
		CH ₄	CH ₃ SH	COS	CO ₂		
12	K ₂ MoO ₄ /NiO/(Ni—SiO ₂) = 25/1.7/(1.5-100)	0.0257	37.63	19.94	42.40	1.127	69.26
13	K ₂ MoO ₄ /CoO/(Ni—SiO ₂) = 25/2.6/(1.5-100)	0.0214	37.64	19.10	43.24	1.148	62.58

TABLE 4

performance of catalysts K ₂ MoO ₄ /Co—SiO ₂ in examples 14-16							
examples	catalysts	Selectivity, %				CO ₂ /CH ₃ SH	CO % conversion
		CH ₄	CH ₃ SH	COS	CO ₂		
14	K ₂ MoO ₄ /(Co—SiO ₂) = (15/4.4-100)	0.01675	42.42	17.05	40.51	0.9550	36.33
15	K ₂ MoO ₄ /NiO/(Co—SiO ₂) = 15/1.0/(1.5-100)	0.01507	46.15	23.66	30.17	0.6538	24.77
16	K ₂ MoO ₄ /CoO/(Co—SiO ₂) = 15/1/(1.5-100)	0.01459	35.74	16.91	34.33	0.7705	24.64

TABLE 5

performance of catalysts K ₂ MoO ₄ —NiO/Ni—SiO ₂ in examples 17-18							
examples	catalysts	Selectivity, %				CO ₂ /CH ₃ SH	CO % conversion
		CH ₄	CH ₃ SH	COS	CO ₂		
17	MoO ₃ /K ₂ O/(Ni—SiO ₂) = 11/4/(4.4-100)	0.0226	45.57	19.91	34.22	0.7466	56.84
18	MoO ₃ /K ₂ O/NiO/Ni—SiO ₂ = 11/4/0.25/(1.5-100)	0.0283	39.55	22.21	38.20	0.9658	60.32

The invention claimed is:

1. A catalyst comprising

- a) a support consisting of a porous carrier and a metal A selected from Ni or Co, wherein the porous carrier is SiO₂ and the metal A is deposited on the carrier by electroless deposition to form an activated metal carrier;

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- b) a Mo—O—K based active component impregnated on the activated metal carrier, wherein the Mo—O—K based active component is K₂MoO₄ or MoO₃ and K₂O; and

- 5 c) optionally an active promoter Me_xO_y, which is impregnated on the activated metal carrier, where Me is Ni or Co, wherein x and y depend on the valence of the metal, and wherein the weight ratios of the catalyst are:

$$K_2MoO_4/Me_xO_y/metalA-carrier=(5-20)/(0.0-25.0)/(0.5-8.0)-100; \text{ or}$$

$$MoO_3/K_2O/Me_xO_y/metalA-carrier=(15-20)/(10-15)/(0.0-25.0)/(0.5-8.0)-100.$$

2. The catalyst according to claim 1, wherein the support comprises reduced Pd and P components.

3. Method of producing the catalyst of claim 1 comprises the steps:

- a) activating a SiO₂ carrier, wherein the activation comprises the steps of first treating the carrier with a solution of a Pd-component and a reducing agent;
- b) impregnating said treated carrier with a solution comprising a solution of a metal salt whereby the metal is chosen from the group comprising Co and Ni, to achieve

- electroless deposition of said metal on the treated carrier to produce the catalyst support;
- c) impregnating said support with an impregnation liquid of an aqueous solution of K_2MoO_4 or $(NH_4)Mo_7O_{24}$ plus a potassium compound or MoO_3 plus a potassium compound; and optionally a precursor of said active promoter Me_xO_y , wherein Me is Ni or Co, followed by drying the received product to obtain the desired catalyst.
4. The process according to claim 3, wherein said support is prepared by electroless plating method, the preparation processes include:
- (i) the preparation of metal-plating solution; a given quantity of soluble metal salt wherein the metal salt is chosen from Ni or Co salt, chosen and a given quantity of coordinating agent are dissolved in given quantity of distilled water successively to produce a metal-plating solution, in which the concentration of the metal ion varies from 1 g/l to 20 g/l, preferably 5-7 g/l; keeping stirring for 10 minutes, then a given quantity of a stabilizing agent are added one after another to the plating solution obtained above, stirring for another 20 minutes, followed by adding some $NH_3 \cdot H_2O$ to adjust the pH of the plating solution to 7.0-13.0, preferably 8.0-12.0; finally, suitable amount of distilled water is used to adjust the volume of the solution in such a way that the concentration of metal salt chosen in the plating solution varies from 1 g/l to 20 g/l, preferably 5-7 g/l;
 - (ii) pretreatment of the SiO_2 carrier chosen comprising the steps of
 - a) the carrier should be washed with distilled water, and then dried, followed by treatment of the clean carrier by immersing it into a solution of $4.5 \text{ mol/l } H_2SO_4 + 0.88 \text{ mol/l } H_2O_2$ (1:1) for 5 minutes under agitating, and then washed with distilled water three times;
 - b) the cleaned carrier is immersed in an aqueous solution of activation agent under agitation, said activation agent is $PdCl_2/HCl$, the concentration of the activation agent varies from 0.05 g/l to 1.0 g/l, preferably from 0.1 g/l to 0.5 g/l; keeping ultrasonically agitating for 30-35 minutes, then washed with distilled water three times;

- c) the activated carrier is immersed in an aqueous solution of reduction agent under agitation, the concentration of the reduction agent varies from 20 g/l to 30 g/l, keeping agitating for 10 seconds;
 - (iii) plating of metal onto carrier is conducted by putting the activated carrier produced in step (2) into the plating solution at 30-90° C. for 30-40 minutes, wherein the metal-plated carrier is washed with distilled water three times and then dried at 110° C. for 6 hours.
5. The process according to claim 3, wherein said reduction agent is $NaH_2PO_3 \cdot H_2O$ or $NaBH_4$.
6. The process according to claim 3, wherein said stabilizing agent is ammonium sulfate or ammonium chloride.
7. The process according to claim 3, wherein said coordinating agent is at least one chosen from $Na_3C_6H_5O_7 \cdot 2H_2O$, $C_6H_8O_7 \cdot H_2O$, $C_2H_8N_2$ or $NaKC_4H_4O_6 \cdot 4H_2O$, the concentration of the chelating agent varies from 1 g/l to 60 g/l.
8. The process according to claim 3, wherein the pH value of the electroless plating solution varies from 7.0 to 13.0, preferably from 8.0 to 12.0.
9. The process according to claim 4, wherein at least one chelating reagent should present in the impregnation solution.
10. The process according to claim 4, wherein the chelating reagent is chosen from the group of citric acid, ammonium citrate tribasic, L-glutamic acid, tartaric acid and ethylenediaminetetraacetic acid (EDTA); and the amount of chelating agent added correspondingly is 0.1-0.6 times as much as that of the support, more preferably is 0.3-0.6 times as much as that of the support.
11. The process according to claim 3, wherein the pH value of the impregnation solution is adjusted to 8-12, preferably 8-10 by ammonia.
12. A method for preparing methyl mercaptan in a catalytic process comprising:
- a) providing the supported catalyst of claim 1; and
 - b) utilizing said catalyst reacting carbon oxides, sulphur and/or hydrogen sulphide and hydrogen to form methyl mercaptan.

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